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USE OF NANOSCALE PARTICLES FOR IMPROVING DIRT REMOVAL

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(57) Abstract: The invention relates to the use of particles with a particle size of 5 to 500 nm for improving the removal of dirt from and/or reducing the re-soiling of surfaces. Said particles can be used for finishing textiles, in textiles detergents and for pre-treating or post-treating textiles in particular.

This invention concerns the use of particles with a particle size from 5 to 500 nm to improve the soil release properties of surfaces and/or to reduce soil redeposition on surfaces.

In the processing of textiles textile finishing plays an important role. By using appropriate auxiliary agents the properties of textiles are changed so that they are easier to take care of. Examples of finishing measures are the improvement of crease recovery and dimensional stability, bleaching and treatment with optical brighteners or dyes, the provision of softening finishes to change the feel, hydrophilizing finishes to improve water absorption behavior. In order to prevent deposition of soil or to make it easier to wash soil out, textiles are given a so-called soil release finish.

Besides this permanent finishing of textiles when they are manufactured some of the described auxiliary agents are also used in textile detergents or pretreatment or aftertreatment agents in order to achieve a temporary use there. For example, the corresponding soil release

polymers are added to detergents and then these polymers result in reduced soil deposition—even that caused by redeposition of released soil during the wash cycle.

Observations in nature demonstrated that the surfaces of plants have soil-releasing properties, since soil particles deposited on these surfaces do not remain there long. In addition, such surfaces are capable of being cleaned by rain or moving water. This effect is due to the wax layers that are found on the surface and in particular to their surface structure.

European Patent EP 0772 514 discloses a plant-mimicking self-cleaning surface for objects, which has an artificial surface structure of elevations and depressions and is characterized by the fact that the distance between the elevations lies in the range from 5 to 200 μm and the height of the elevations lies in the range from 5 to 100 μm and at least the elevations consist of hydrophobic polymers and permanently hydrophobic materials and the elevations are not removed by water or by water that contains detergents.

The textiles known from the prior art have a permanently modified surface. Permanent modification of textile surfaces is not always desirable, especially in the clothing field. On the one hand, the consumer wants natural textiles, with the favorable properties that these textiles are considered to have, and, on the other hand these textiles should have the advantages of synthetic textiles as far as possible with regard to care properties.

This invention was based on the task of making available a detergent or pretreatment or aftertreatment agent that is suitable for modifying surfaces, especially temporarily, so that an improvement of the releaseability of soil is achieved and the surface is temporarily given soil-release properties. Another task is to achieve the desired improvement in particular for textile surfaces, preferably for natural materials like cotton.

It was surprisingly found that through the use of particles with a particle size from 5 to 500 nm [on] surfaces, i.e., both hard and textile surfaces, a clear improvement of hydrophilicity is achieved and thus the soil release from the surfaces is also improved and soil release properties can be temporarily conferred to them. Through the use of the particles a structurizing of the surface is brought about, through which, for example in the case of textiles, especially cotton or cotton blends, the above-described effects arise.

Temporary modification in the sense of this invention means that the effect can be maintained for a few, especially up to 4, washing or cleaning cycles.

Accordingly, the object of the invention is the use of particles with a particle size from 5 to 500 nm to improve the soil release properties of surfaces and/or to reduce the soil redeposition on surfaces.

The particles used in accordance with the invention are preferably particles that are insoluble or only slightly soluble in water and that temporarily remain on the textile. In accordance with the invention, these particles have a particle size from 5 to 500 nm, preferably

from 5 to 250 nm. Because of their particle size these particles are also called nanoscale particles. Any insoluble solids that occur in said size distribution can be used as particles. Examples of suitable particles are all precipitation silicas, aerogels, xerogels, $\text{Mg}(\text{OH})_2$, boehmite ($\text{Al}(\text{O})\text{OH}$), ZrO_2 , ZnO , CeO_2 , Fe_2O_3 , Fe_3O_4 , TiN , hydroxyapatite, bentonite, hectorite, $\text{SiO}_2\text{:CeO}_2$ (SiO_2 doped with CeO_2), SnO_2 , $\text{In}_2\text{O}_3\text{:SnO}_2$, MgAl_2O_4 , HfO_2 , sols like SiO_2 sols, Al_2O_3 sols or TiO_2 sols, as well as any mixtures of these.

Surfaces in the sense of this invention are any hard or textile surfaces that are to be treated. Hard surfaces that may be mentioned are in particular the surfaces of stone, ceramic, wood, plastic, metal such as stainless steel, including floorcoverings like carpets, etc., that are found in homes. Textile surfaces include all synthetic and natural textiles, where the particles used in accordance with the invention are preferably used to treat cotton and cotton blends.

In one particularly preferred embodiment of this invention the particles are used in agents for treating textiles, especially for textile pretreatment and also as textile aftertreatment and for textile washing. The particles can also be used in textile treatment in the textile industry, where the particles can be used both for permanent and also for temporary textile treatment.

The content of these nanoscale particles in such agents should be calculated so that the surface, especially the textile surface, is sufficiently covered. Preferably the agents contain 0.01-35 wt%, especially preferably 0.01-20 wt% and in particular 0.5-10 wt% of the nanoscale particles, with respect to the ready-to-use agent.

The concentration of the nanoscale particles used in accordance with the invention in the application solution is preferably between 0.001 and 10 wt%, in particular between 0.01 and 2 wt%, with respect to the application solution. The pH of the application solution is preferably between 6 and 12, especially between 7 and 10.5. Particularly good results with respect to redeposition and soil release are achieved in this pH range.

A further improvement in soil release and reduction of redeposition can be achieved if the surface of the nanoscale particles is modified. This can take place, for example, through conventional complexing agents, so that the precipitation of Ca or Mg salts can be prevented. These compounds can be applied in an amount such that they are contained in the ready-to-use agent in amounts from 1 to 8 wt%, preferably 3.0 to 6.0 wt%, and especially 4.0 to 5.0 wt%, with respect to the ready-to-use agent. Usually they are situated on the surface of the particles.

One preferred class of complexing agents consists of the phosphonates. Among these preferred compounds are, especially, organophosphates such as 1-hydroxyethane-1,1-diphosphonic acid (HEDP), aminotri(methylenephosphonic acid) (ATMP), diethylenetriamine-penta(methylenephosphonic acid) (DTPMP, DETPMP), and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBS-AM), which are for the most part used in the form of their ammonium or alkali metal salts. The phosphonates are applied to the surface of the

particles in an amount such that they are contained in the ready-to-use agent in amounts from 0.01 to 2.0 wt%, preferably 0.05 to 1.5 wt%, and especially from 0.1 to 1.0 wt%.

In addition, it is possible to use substances that complex heavy metals as complexing agents. Suitable heavy metal complexing agents are, for example, ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) in the form of the free acids or as alkali metal salts and derivatives of them, as well as alkali metal salts of anionic polyelectrolytes like polymaleates and polysulfonates.

Other suitable complexing agents are low-molecular hydroxycarboxylic acids like citric acid, tartaric acid, malic acid, lactic acid or gluconic acid, or their salts, with citric acid and sodium citrate being particularly preferred.

The modification of the particle surface can take place, for example, by simple stirring of the suspension of the particles together with the complexing agent, which absorbs onto the surface of the particles during the stirring.

For the specialist it is obvious that the total amount of complexing agents that are supposed to be incorporated into the [finishing] agents does not have to be applied to the nanoscale particles. It is also possible to incorporate these compounds directly, entirely or partially.

A further increase of the wettability of the surfaces to be treated can also be achieved through the addition of hydrophilizing agents. Examples of such hydrophilizing agents are monohydric or polyhydric alcohols, alkanolamines or glycol ethers, provided they are miscible with water. Preferably the hydrophilizing agents are chosen from ethanol, n-propanol, isopropanol, butanols, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ethers, dipropylene glycol monomethyl or ethyl ethers, diisopropylene glycol monomethyl or monoethyl ethers, methoxy-, ethoxy- or butoxy triglycols, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol t-butyl ether, alcohols, especially C₁-C₄ alkanols, glycols, polyethylene glycols, preferably with a molecular weight between 100 and 100,000, especially between 200 and 10,000, and polyols like sorbitol and mannitol, and polyethylene glycol that is liquid at room temperature, carboxylic acid esters, polyvinyl alcohols, ethylene oxide-propylene oxide block copolymers as well as any mixtures of these.

The particles used in accordance with the invention can be incorporated into agents that are in liquid to gel form or even in solid form.

If the agents are in liquid to gel form, as a rule these are aqueous preparations that contain still other water-miscible organic solvents and thickeners. Among the water-miscible organic solvents are, for example, the compounds mentioned above [as] hydrophilizing agents. The

preparation of liquid to gel preparations can take place continuously or batchwise by simple mixing of the components, optionally at elevated temperature.

To adjust the viscosity one or more thickener systems can be added to a liquid composition. The viscosity of liquid to gel compositions can be measured by standard techniques (for example the Brookfield viscosimeter RVD-VII at 20 rpm and 20°C, spindle 3) and is preferably in the range from 100 to 5000 mPas. Preferred compositions have viscosities from 200 to 4000 mPas, with values between 400 and 2000 mPas being particularly preferred.

Suitable thickeners are inorganic or polymer organic compounds. Mixtures of several additives can also be used.

Among the inorganic thickeners are, for example, polysilicic acids, clay minerals like montmorillonite, zeolites, silicas and bentonites.

The organic thickeners derive from the group of the natural polymers, the modified natural polymers and fully synthetic polymers. These substances, which are also called swell(ing) agents and are for the most part high molecular substances, absorb the liquids, swell in doing so and in the end convert to viscous true or colloidal solutions.

Polymers that derive from nature and are used as rheological additives are, for example, agar agar, carrageen, traganth, gum arabic, alginates, pectins, polyoses, guar flour, carob flour, starches, dextrans, gelatins and casein.

Modified natural substances derive above all from the group of the modified starches and celluloses, for example, here one may mention carboxymethylcellulose and other cellulose ethers, hydroxyethyl and hydroxypropylcelluloses as well as germ meal ethers.

A large group of thickeners that are widely used in many areas are the fully synthetic polymers like polyacrylic and polymethacrylic compounds, vinyl polymers, polycarboxylic acids, polyethers, polyimines, polyamides and polyurethanes.

The thickeners can be contained in an amount up to 10 wt%, preferably from 0.05 to 5 wt%, and especially preferably from 0.1 to 3 wt%, with respect to the ready-to-use composition.

Moreover, it is also possible to use surfactant thickeners, for example alkyl polyglycosides like C₈₋₁₀ alkyl polyglucoside (APG® 220, Henkel KGaA); C₁₂₋₁₄ alkyl polyglucoside (APG® 600, Henkel KGaA).

Among the agents in solid form are powders, compacted materials like granulates and molded articles (tablets). The individual forms can be produced by the methods known from the prior art such as spray drying, granulation and compression molding.

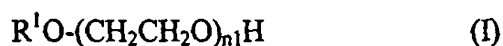
The particles that are used in accordance with the invention can be used especially in combination with surfactants, which are preferably selected from nonionic, anionic, amphoteric and cationic surfactants as well as any mixtures of these.

The surfactants are preferably present in an amount from 0.1 to 50 wt%, preferably from 0.1 to 35 wt%, and especially from 0.1 to 15 wt%, with respect to the composition.

Alkoxylated, advantageously ethoxylated, especially primary alcohols with preferably 8 to 18 C atoms and an average of 1-12 mol ethylene oxide (EO) per mol of alcohol, in which the alcohol residue can be linear or preferably methyl-branched in position 2 or can contain linear and methyl-branched residues in a mixture, as are usually present in oxo alcohol residues, are preferably used as nonionic surfactants. In particular, however, alcohol ethoxylates with linear residues of alcohols of natural origin with 12-18 C atoms, for example from coconut, palm, tallow or oleyl alcohol, and an average of 2-8 EO per mol of alcohol are preferred. Among the preferred ethoxylated alcohols are, for example, C₁₂₋₁₄ alcohols with 3 EO to 7 EO, C₉₋₁₁ alcohol with 7 EO, C₁₃₋₁₅ alcohols with 3 EO, 5 EO, 7 EO or 8 EO, C₁₂₋₁₈ alcohols with 3 EO, 5 EO or 7 EO and mixtures of these alcohols such as mixtures of C₁₂₋₁₄ alcohol with 3 EO and C₁₂₋₁₈ alcohol with 7 EO. Said degrees of ethoxylation are statistical averages that for a particular product can be a whole number or a fraction. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants fatty alcohols with more than 12 EO can also be used. Examples of these are tallow fatty alcohol with 14 EO, 25 EO, 30 EO or 40 EO. Nonionic surfactants that contain EO and PO groups together in the molecule can also be used in accordance with the invention. Here block copolymers with EO-PO block units or PO-EO block units can be used, but EO-PO-EO copolymers or PO-EO-PO copolymers can also be used. Of course, mixed alkoxylated nonionic surfactants in which EO and PO units are not blockwise, but rather statistically distributed, can also be used. Such products are obtained by the simultaneous action of ethylene and propylene oxides on fatty alcohols.

Especially preferred examples of nonionic surfactants that give water on hard surfaces good run off behavior are the fatty alcohol polyethylene glycol ethers, fatty alcohol polyethylene/polypropylene glycol ethers and mixed ethers, which can optionally be blocked end group.

Examples of fatty alcohol polyethylene glycol ethers are ones of formula (I)



in which R¹ stands for a linear or a branched alkyl and/or alkenyl residue with 6-22, preferably 12-18 carbon atoms and n1 stands for numbers from 1 to 5.

Said substances are known commercial products. Typical examples are addition products of an average of 2 or 4 mol ethylene oxide to industrial C_{12/14} coco fatty alcohol (Dehydol® LS-2 or LS-4, Henkel KGaA) or addition products with an average of 4 mol ethylene oxide to C_{14/15}

oxo alcohols (Dobanol® 45-4, Shell). The products can have conventional or narrow homolog distribution.

Fatty alcohol polyethylene/polypropylene glycol ethers are understood to be nonionic surfactants of the formula (II),



in which R^2 stands for a linear or a branched alkyl and/or alkenyl residue with 6-22, preferably 12-18 carbon atoms, $n2$ stands for numbers from 1 to 0 [sic] and $m2$ stands for numbers from 1 to 4.

These substances are also known commercial products. Typical examples are addition products of an average of 5 mol ethylene oxide and 4 mol propylene oxide to industrial $\text{C}_{12/14}$ coco fatty alcohol (Dehydol® LS-54, Henkel KGaA) or 6.4 mol of ethylene oxide and 1.2 mol propylene oxide to industrial $\text{C}_{10/14}$ coco fatty alcohol (Dehydol® LS-980, Henkel KGaA).

Mixed ethers are understood to be end group blocked fatty alcohol polyglycol ethers of the formula (III)



in which R^3 stands for a linear or branched alkyl and/or alkenyl residue with 6-22, preferably 12-18 carbon atoms, $n3$ stands for numbers from 1 to 10, $m3$ stands for 0 or numbers from 1 to 4 and R^4 stands for an alkyl residue with 1-4 carbon atoms or a benzyl residue.

Typical examples are mixed ethers of formula (III) in which R^3 stands for an industrial $\text{C}_{12/14}$ coco alkyl residue, $n3$ stands for 5 or 10, $m3$ for 0 and R^4 for a butyl group (Dehypon® LS-54 or LS-104, Henkel KGaA). The use of butyl- or benzyl-blocked mixed ethers is particularly preferred for reasons of process engineering.

Hydroxyalkylpolyethylene glycol ethers are understood to be compounds of the general formula (IV)



in which

R^5 stands for hydrogen or a straight-chain alkyl residue with 1-16 carbon atoms,

R^6 stands for a straight-chain or branched alkyl residue with 4-8 carbon atoms,

R^7 stands for hydrogen or an alkyl residue with 1-16 carbon atoms and

$n4$ stands for a number from 7 to 30

with the stipulation that the total number of carbon atoms in R^5 and R^7 is 6-16.

In addition, alkyl glycosides of the general formula $RO(G)_x$, in which R means a primary straight-chain or methyl branched, especially methyl-branched in position 2, aliphatic residue with 8-22, preferably 12-18 C atoms and G is the symbol for a glucose unit with 5 or 6 C atoms, preferably glucose, can also be used as other nonionic surfactants. The degree of oligomerization x, which gives the distribution of monoglycosides and oligoglycosides, can be any number between 1 and 10; preferably x is 1.2 to 1.4.

Another class of nonionic surfactants that can be used in particular in solid agents consists of the alkoxyated, preferably ethoxylated or ethoxylated and propoxylated fatty acid alkyl esters, preferably with 1-4 carbon atoms in the alkyl chain.

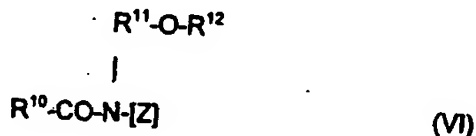
Nonionic surfactants of the type of the amine oxides, for example, N-cocoalkyl-N,N-dimethylamine oxide and N-tallow alkyl-N,N-dihydroxyethylamine oxide, and the fatty acid alkanolamides can also be suitable. The amount of these nonionic surfactants is preferably no more than that of the ethoxylated fatty alcohols, especially no more than half thereof.

Other suitable surfactants are polyhydroxy fatty acid amides of formula (V),



in which R^8CO stands for an aliphatic acyl residue with 6-22 carbon atoms, R^9 stands for hydrogen, an alkyl or hydroxyalkyl residue with 1-4 carbon atoms and [Z] stands for a linear or branched polyhydroxyalkyl residue with 3-10 carbon atoms and 3-10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances, which can usually be obtained by reductive amination of a reducing sugar with ammonia, an alkyl amine or an alkanolamine, followed by acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of the polyhydroxy fatty acid amides also includes compounds of formula (VI),



in which R^{10} stands for a linear or branched alkyl or alkenyl residue with 7-12 carbon atoms, R^{11} stands for a linear, branched or cyclic alkyl residue or an aryl residue with 2-8 carbon atoms and R^{12} stands for a linear, branched or cyclic alkyl residue or an aryl residue or an oxyalkyl residue with 1-8 carbon atoms, where C_{1-4} alkyl or phenyl residues are preferred, and [Z] stands for a

linear polyhydroxyalkyl residue whose alkyl chain is substituted with at least two hydroxyl groups, or alkoxyated, preferably ethoxyated or propoxyated, derivatives of this residue.

[Z] is preferably obtained by reductive amination of a sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds can then be converted to the desired polyhydroxy fatty acid amides by following the teaching of International Patent Application WO-A-95/07331, through the reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst.

Surfactants of the type of the sulfonates and sulfates, for example, are used as anionic surfactants. Possibilities as surfactants of sulfonate type are preferably C₉₋₁₃ alkylbenzene sulfonates, olefin sulfonates, i.e., mixtures of alkene and hydroxyalkane sulfonates and disulfonates, as are obtained, for example, from C₁₂₋₁₈ monoolefins with terminal or internal double bonds by sulfonation with gaseous sulfur trioxide followed by alkali or acid hydrolysis of the sulfonation product. Also suitable are alkane sulfonates, which are obtained from C₁₂₋₁₈ alkanes, for example by sulfochlorination or sulfoxidation followed by hydrolysis or neutralization, respectively. Likewise the esters of α -sulfo [sic; α - sulfo] fatty acids (ester sulfonates), for example the α -sulfonated methyl esters of hydrogenated coco, palm or tallow fatty acids are also suitable.

The alkali and especially the sodium salts of the sulfuric acid semiesters of C₁₂-C₁₈ fatty alcohols, for example from coco fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or the C₁₀-C₂₀ oxo alcohols and those semiesters of secondary alcohols of these chain lengths are preferred as alk(en)yl sulfates. Also preferred are alkenyl sulfates of the said chain length that contain a synthetic straight-chain alkyl residue prepared from petrochemical raw materials. From the standpoint of commercial laundry interests the C₁₂-C₁₆ alkyl sulfates and C₁₂-C₁₅ alkyl sulfates as well as C₁₄-C₁₅ alkyl sulfates are preferred. 2,3-Alkyl sulfates, which are prepared, for example, in accordance with US Patent 3,234,258 or 5,075,041 and can be obtained as commercial product from the Shell Oil Company under the trade name DAN®, are also suitable anionic surfactants.

Other suitable anionic surfactants are sulfonated fatty acid glycerol esters. Fatty acid glycerol esters are understood to mean the mono-, di- and triesters and their mixtures, as are obtained industrially by esterification of a monoglycerol with 1-3 mol fatty acid or in the transesterification of triglycerides with 0.3-2 mol glycerol. Preferred sulfonated fatty acid glycerol esters in this case are the sulfonation products of saturated fatty acids with 6-22 carbon atoms, for example caproic, caprylic, capric, myristic, lauric, palmitic, stearic or behenic acids.

Also, the sulfuric acid monoesters of straight-chain or branched C₇₋₂₁ alcohols ethoxyated with 1-6 mol ethylene oxide, such as 2-methyl-branched C₉₋₁₁ alcohols with an average of 3.5 mol ethylene oxide (EO) or C₁₂₋₁₈ fatty alcohols with 1-4 EO, are suitable. They

are used in cleaning agents because of their high foaming capacity in only relatively small amounts, for example in amounts from 1 to 5 wt%.

Other suitable anionic surfactants are also the salts of alkylsulfosuccinic acids, which are also called sulfosuccinates or sulfosuccinic acid esters, and the monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and especially ethoxylated fatty alcohols. Preferred sulfosuccinates contain C₈₋₁₈ fatty alcohol residues or mixtures of them. Especially preferred sulfosuccinates contain a fatty alcohol residue that derives from ethoxylated fatty alcohols which, taken as such, are nonionic surfactants (description, see below). Here again sulfosuccinates whose fatty alcohol residues derive from ethoxylated fatty alcohols with narrow homolog distribution are especially preferred. It is also possible to use alkenylsuccinic acid with preferably 8-18 carbon atoms in the alk(en)yl chain or its salts.

Other anionic surfactants that are possibilities are soaps, which are used especially in powdered agents and at high pH values. Saturated and unsaturated fatty acid soaps like the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid and especially of natural fatty acids, for example coco, palm, olive oil or tallow fatty acids and derived soap mixtures, are suitable.

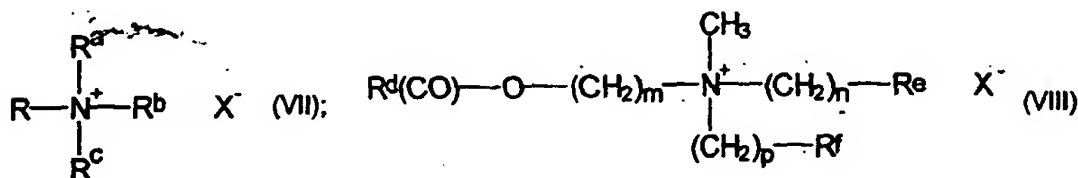
The anionic surfactants, including the soaps, can be in the form of their sodium, potassium or ammonium salts and as soluble salts of organic bases such as mono-, di- or triethanolamine. Preferably the anionic surfactants are in the form of their sodium or potassium salts, especially in the form of the sodium salts.

The so-called gemini surfactants are also possible as other surfactants. These in general are understood to be those compounds that have two hydrophilic groups and two hydrophobic groups per molecule. As a rule these groups are separated from each other by a so-called "spacer." As a rule, this spacer is a carbon chain, which should be long enough that the hydrophilic groups are far enough apart that they can react independently of each other. Such surfactants are generally characterized by an unusually low critical micelle concentration and the ability to reduce the surface tension of water greatly. In exceptional cases, however, not only dimer, but also trimer surfactants are understood under the term gemini surfactants.

Suitable gemini surfactants are, for example, sulfated hydroxy mixed ethers of dimer alcohol bis- and trimer alcohol trisulfates and ether sulfates. End group blocked dimer and trimer mixed ethers are characterized in particular by their bi- and polyfunctionality. For instance said end group blocked surfactants have good wetting properties and are low-foaming, so that they are particularly suitable for use in machine washing or cleaning processes. However, gemini polyhydroxy fatty acid amides or polypolyhydroxy fatty acid amides can also be used.

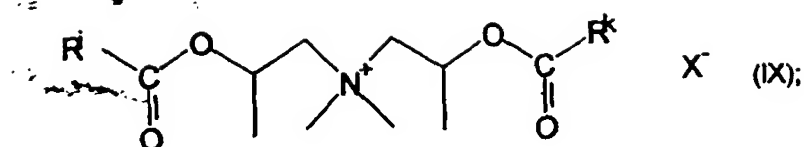
Examples of cationic surfactants are quaternary ammonium compounds, cationic polymers and emulsifiers, such as are used in hair care agents and in agents for textile finishing.

Suitable examples are quaternary ammonium compounds of formulas (VII) and (VIII),



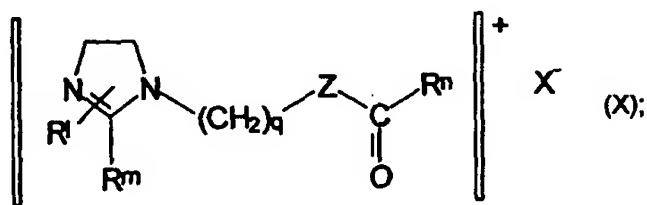
where in (VII) R and R^a stand for an acyclic alkyl residue with 12-24 carbon atoms, R^b stands for a saturated C₁-C₄ alkyl or hydroxyalkyl residue, R^c is either equal to R, R^a or R^b or stands for an aromatic residue. X⁻ stands either for a halide, methosulfate, methophosphate or phosphate ion or mixtures of these. Examples of cationic compounds of formula (VII) are didecyldimethylammonium chloride, ditallowdimethylammonium chloride or dihexadecylammonium chloride.

Compounds of formula (VIII) are the so-called ester quats. Ester quats are characterized by excellent biodegradability. Here R^d stands for an aliphatic acyl residue with 12-22 carbon atoms and 0, 1, 2 or 3 double bonds; R^e stands for H, OH or O(CO)R^f, R^g, independent of R^f, stands for H, OH or O(CO)R^h, where R^g and R^h, independently, each stand for an aliphatic acyl residue with 12-22 carbon atoms and 0, 1, 2 or 3 double bonds. m, n and p can each independently have the value 1, 2 or 3. X⁻ can be either a halide, methosulfate, methophosphate or phosphate ion or mixtures of these. Compounds that contain the group O(CO)R^g for R^d and alkyl residues with 16-18 carbon atoms for R^d and R^g are preferred. Especially preferred are compounds in which R^f additionally stands for OH. Examples of compounds of formula (VIII) are methyl-N-(2-hydroxyethyl)-N,N-di(tallowacyloxyethyl)ammonium methosulfate, bis(palmitoyl)ethylhydroxyethylmethylammonium methosulfate or methyl-N,N-bis(acyloxyethyl)-N-(2-hydroxyethyl)ammonium methosulfate. If quaternized compounds of formula (VIII) that have unsaturated alkyl chains are used, the acyl groups whose corresponding fatty acids have an iodine number between 5 and 80, preferably between 10 and 60 and especially between 15 and 45 and that have a cis/trans isomer ratio (in wt%) greater than 30:70, preferably greater than 50:50 and especially greater than 70:30, are preferred. Commercial examples are the methylhydroxyalkyldialkoyloxyalkylammonium methosulfates sold by Stepan under the trade name Stepan[®] or the products from Cognis known as Dehyquat[®] or the products from Goldschmidt-Witco known as Rewoquat[®]. Other preferred compounds are the diester quats of formula (IX) which are obtainable under the name Rewoquat[®] W 222 LM or CR 3099 and in addition to softness provide for stability and color protection.



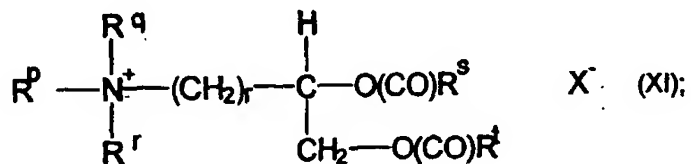
R^j and R^k independently each stand for an aliphatic acyl residue with 12-22 carbon atoms and 0, 1, 2 or 3 double bonds.

Besides the quaternary compounds described above, it is also possible to use other known compounds such as quaternary imidazolinium compounds of formula (X),



where R^l stands for H or a saturated alkyl residue with 1-4 carbon atoms, R^m and R^n independently each can stand for an aliphatic, saturated or unsaturated alkyl residue with 12-18 carbon atoms, R^m alternatively can also stand for $\text{O}(\text{CO})\text{R}^o$, where R^o means an aliphatic, saturated or unsaturated alkyl residue with 12-18 carbon atoms, and Z means an NH group or oxygen, and X^- is an anion. q can take on any integer value between 1 and 4.

Other suitable quaternary compounds are described by formula (XI),



where R^p , R^q and R^r independently stand for a C_{1-4} alkyl, alkenyl or hydroxyalkyl group, R^s and R^t independently represent a C_{8-28} alkyl group and r is a number between 0 and 5.

Besides the compounds of formulas (VII) and (VIII), it is also possible to use short-chain water-soluble quaternary ammonium compounds such as trihydroxyethylmethylammonium methosulfate or the alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides

and trialkylmethylammonium chlorides, for example cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyltrimethylammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride.

Protonated alkylamine compounds that have softening action and the unquaternized protonated precursors of cationic emulsifiers are also suitable.

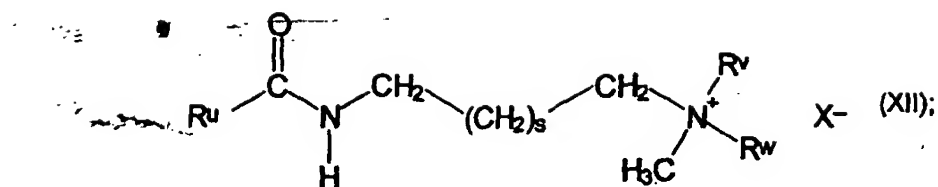
Other cationic compounds that can be used in accordance with the invention are the quaternized protein hydrolyzates.

Among the suitable cationic polymers are the polyquaternium polymers as [described] in the CTFA Cosmetic Ingredient Dictionary (The Cosmetic, Toiletry and Fragrance [Association], Inc., 1997), especially the polyquaternium 6, polyquaternium 7 and polyquaternium 10 polymers that are called merquats (Ucare Polymer IR 400; Amerchol), polyquaternium 4 copolymers such as graft copolymers with a cellulose backbone and quaternary ammonium groups that are bonded via an alkyltrimethylammonium chloride, cationic cellulose derivatives like cationic guar, guar hydroxypropyltrimethylammonium chloride and similar quaternized guar derivatives (for example Cosmedia Guar, Cognis GmbH), cationic quaternary sugar derivatives (cationic alkyl polyglucosides), for example the commercial product Glucquat® 100, according to CTFA nomenclature a "lauryl methyl gluceth-10 hydroxypropyl dimonium chloride," copolymers of PVP and dimethylaminomethacrylate, copolymers of vinyl imidazole and vinylpyrrolidone, aminosilicone polymers and copolymers.

Quaternary polymers (for example Luviquat Care, BASF) and cationic biopolymers based on chitin and its derivatives, for example the polymer obtainable under the trade name Chitosan® (Cognis) can also be used.

Cationic silicone oils such as the commercially available products Q2-7224 (Dow Corning; a stabilized trimethylsilylamodimethicone), Dow Corning 929 emulsion (containing a hydroxylamino modified silicone, which is also called amodimethicone), SM-2059 (General Electric), SLM-55067 (Wacker) Abil®-Quat 3270 and 3272 (Goldschmidt-Rewo; diquaternary polydimethylsiloxanes, Quaternium-80), and silicone quat Rewoquat® SQ 1 (Tegopren® 6922, Goldschmidt-Rewo) are also suitable in accordance with the invention.

Compounds of formula (XII) are also suitable,



which can be alkyl amidoamines in their unquaternized or, as shown, their quaternized form. R^u can be an aliphatic acyl residue with 12-22 carbon atoms and 0, 1, 2 or 3 double bonds. s can take on values between 0 and 5. R^v and R^w independently each stand for H, C_{1-4} alkyl or hydroxyalkyl. Preferred compounds are fatty acid amidoamines like the stearylamidopropyldimethylamine obtainable under the name Tego Amide® S 18 or the 3-tallowamidopropyl trimethylammonium methosulfate obtainable under the name Stepantex® X 9124, which are characterized by color transfer inhibiting effect and particularly by their good biodegradability, in addition to a good conditioning action.

The particles used in accordance with the invention are preferably incorporated into agents for textile finishing, textile detergents, textile pretreatment agents or textile aftertreatment agents.

Another object of this invention is accordingly, agents for textile treatment that are characterized by the fact that they contain particles with a particle size from 5 to 500 nm to improve soil release of and/or to reduce soil redeposition on textile surfaces.

The agents can contain, besides the particles used in accordance with the invention, the above described surfactants as well as other components, such as are usually used in detergents and cleaning agents.

Possibilities as other components are, for example, builders, especially zeolites, silicates, carbonates, organic builders and, where there are no ecological proscriptions against their use, the phosphates, too.

Suitable crystalline layer sodium silicates have the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot \text{H}_2\text{O}$, where M means sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20, and preferred values for x are 2, 3 or 4. Preferred crystalline layer silicates of this formula are ones in which M stands for sodium and x takes on the values 2 or 3. In particular, both β - and δ -sodium disilicates $\text{Na}_2\text{Si}_2\text{O}_5 \cdot y\text{H}_2\text{O}$ are preferred.

Also usable are amorphous sodium silicates with an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8 and especially from 1:2 to 1:2.6, which are slow dissolving substances and have secondary detergent properties. The delayed dissolution, compared to traditional amorphous sodium silicates, can be produced in various ways, for example by surface

treatment, compounding, compaction/densification or by superdrying. Within the scope of this invention the term "amorphous" is also understood to mean "X-ray amorphous." This means that in X-ray diffraction experiments the silicates do not produce sharp X-ray reflections as are typical for crystalline substances, but rather produce at most one or more peaks of the scattered X-ray radiation that have a width of several degrees of the diffraction angle. However, particularly good builder properties can very probably also be obtained if the silicate particles produce overlapping or even sharp diffraction peaks in electron diffraction experiments. This should be interpreted to mean that the products have microcrystalline regions on the order of 10 to a few hundredths of nm in size, where values up to a maximum of 50 nm and especially up to a maximum of 20 nm are preferred. Especially preferred are compacted amorphous silicates, compounded amorphous silicates and superdried X-ray amorphous silicates.

The finely crystalline synthetic zeolite containing bound water that is used is preferably zeolite A and/or P. Zeolite MAP® (commercial product of the Crosfield company) is particularly preferred as zeolite P. However, zeolite X as well as mixtures of A, X and/or P are also suitable.

Other zeolites that are preferably used and particularly suitable are zeolites of the faujasite type. Together with zeolites X and Y the mineral faujasite belongs to the faujasite type within the zeolite structural group 4, which is characterized by the dihexacycle subunit D6R (see Donald W. Breck: "Zeolite Molecular Sieves," John Wiley & Sons, New York, London, Sydney, Toronto, 1974, page 92). Besides the said faujasite types the zeolite structural group 4 also includes the minerals chabazite and gmelinite and the synthetic zeolites R (chabazite type), S (smelinite type), L and ZK-5. The last two synthetic zeolites do not have any mineral analogs.

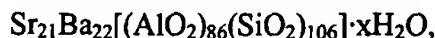
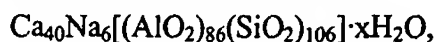
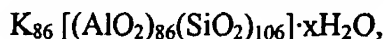
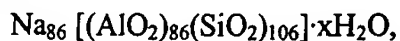
Zeolites of faujasite type are formed of β -cages that are tetrahedrally joined via D6R subunits, where the β cages are arranged similarly to the carbon atoms in diamonds. The three-dimensional network of these faujasite type zeolites has pores 2.2 and 7.4 Å in size, the elementary cell additionally contains 8 cavities with about 13 Å diameter and can be described by the formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$. The network of zeolite X contains a void volume of roughly 50% with respect to the dehydrated crystal, which represents the greatest empty space of all of the known zeolites (zeolite Y: about 48% void volume, faujasite: about 47% void volume). (All data from: Donald W. Breck: "Zeolite Molecular Sieves," John Wiley & Sons, New York, London, Sydney, Toronto, 1974, pp. 145, 176, 177).

Within the scope of this invention the term "zeolite of faujasite type" characterizes all three zeolites that form the faujasite subgroup of the zeolite structural group 4. Besides zeolite X, zeolite Y and faujasite as well as mixtures of these compounds can also be used, with the pure zeolite X being preferred.

Mixtures or cocrystallizates of zeolites of faujasite type with other zeolites, which do not necessarily have to belong to zeolite structural group 4, can also be used.

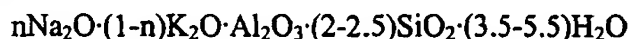
Aluminosilicates, which can also be used, are commercially available and the methods for preparation of them are described in standard monographs.

Examples of commercially available zeolites of type X can be described by the following formulas:



in which x can take on values between 0 and 276 and which have pore sizes from 8.0 to 8.4 Å.

Commercially available and preferably usable within the scope of this invention is, for example, also a cocrystallizate of zeolite X and zeolite Y (about 80 wt% zeolite X), which is sold by the company Condea Augusta S.p.A. under the trade name Vegobond AX® and can be described by the formula



The zeolite can be used both as a builder in a granular compound and can also be used for a kind of "powdering" of the entire mixture that is to be pressed, with usually both methods for incorporating the zeolite into the premix being used. Suitable zeolites have an average particle size of less than 10 µm (volume distribution; measurement method: Coulter counter) and preferably contain 18-22 wt%, especially 20-22 wt%, bound water.

Of course, the use of the generally known phosphates as builder substances is also possible, provided such use should not be avoided for ecological reasons. Among the many commercially available phosphates the alkali metal phosphates, hydrogen phosphates and dihydrogen phosphates, with particular reference to pentasodium and pentapotassium triphosphate (sodium or potassium tripolyphosphate) having the greatest importance in the detergent and cleaning agent industry.

The term alkali metal phosphates here is the overall designation for the alkali metal (especially sodium and potassium) salts of the various phosphoric acids, among which one can distinguish metaphosphoric acids $(\text{HPO}_3)_n$ and orthophosphoric acid H_3PO_4 in addition to higher molecular representatives. The phosphates combine several advantages: they act as alkali carriers, prevent calcium deposits on machine parts or lime encrustations in fabrics and beyond this they contribute to cleaning power.

Especially polycarboxylates/polycarboxylic acids, polymer polycarboxylates, aspartic acid, polyacetals, dextrans, other organic cobuilders (see below) and phosphonates can be used as organic cobuilders. These classes of substances are described below.

Usable organic builder substances are, for example, the polycarboxylic acids that can be used in the form of their sodium salts, where polycarboxylic acids are understood to mean those

carboxylic acids that have more than one acid function. For example, these are citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), provided there is no restriction to such use for ecological reasons, as well as mixtures of these substances. Preferred salts are the salts of the polycarboxylic acids like citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures of these.

Also the acids themselves can be used. Besides their builder action, the acids typically also have the property of an acidulation component and thus also serve to establish a low and mild pH value for detergents or cleaning agents. Citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and any mixtures of these should be named in particular here.

Further, polymer polycarboxylates are suitable as builders, for example the alkali metal salts of polyacrylic acid or polymethacrylic acid, for example ones with a relative molecular weight from 500 to 70,000 g/mol.

The molecular weights given for the polymer polycarboxylates in the sense of this document are weight average molecular weights M_w of the relevant acid form, which were basically determined by means of gel permeation chromatography (GPC), using a UV detector. The measurement was made against an external polyacrylic acid standard, which affords realistic molecular weight values because of its structural relationship to the tested polymers. These data clearly deviate from the molecular weight data in which polystyrene sulfonic acids are used as standard. The molecular weights measured against polystyrene sulfonic acids as a rule are clearly higher than the molecular weights given in this document.

Suitable polymers are especially polyacrylates, which preferably have a molecular weight from 2000 to 20,000 g/mol. Because of their superior solubility, again the short-chain polyacrylates that have molecular weights from 2000 to 10,000 g/mol, and especially preferably from 3000 to 5000 g/mol, can be preferred from this group.

Also suitable are copolymer polycarboxylates, especially those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid. Copolymers of acrylic acid with maleic acid that contain 50-90 wt% acrylic acid and 50-10 wt% maleic acid proved to be particularly suitable. Their relative molecular weight with respect to free acids is in general 2000-70,000 g/mol, preferably 20,000-50,000 g/mol and especially 30,000-40,000 g/mol.

The (co)polymer polycarboxylates can be used either as powders or as aqueous solutions. The content of the (co)polymer polycarboxylates in the agents is preferably 0.5-20 wt%, especially 3-10 wt%.

The polymers can also contain allylsulfonic acids such as allyloxybenzenesulfonic acid and methallylsulfonic acid as monomer, for an improvement of water solubility.

Also especially preferred are biodegradable polymers of more than two different monomer units, for example those that contain as monomers salts of acrylic acid and maleic acid and vinyl alcohol or vinyl alcohol derivatives or that contain as monomers salts of acrylic acid and 2-alkylallylsulfonic acid as well as sugar derivatives.

Other preferred copolymers are those that contain acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers.

Polymer aminodicarboxylic acids, their salts or their precursors may also be mentioned as other preferred builder substances. Polyaspartic acids or their salts and derivatives are especially preferred.

Other suitable builder substances are polyacetals, which can be obtained by the reaction of dialdehydes with polyolcarboxylic acids that have 5-7 carbon atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes like glyoxal, glutaraldehyde, terephthaldehyde and their mixtures and from polyol carboxylic acids like gluconic acid and/or glucoheptonic acid.

Other suitable organic builder substances are dextrans, for example oligomers or polymers of carbohydrates, which can be obtained by partial hydrolysis of starches. The hydrolysis can be carried out by conventional methods, for example acid- or enzyme-catalyzed methods. Preferably these are hydrolysis products with average molecular weights in the range from 400 to 500,000 g/mol. A polysaccharide with a dextrose equivalent (DE) in the range of 0.5-40, especially 2-30, is preferred, where DE is a conventional measure of the reducing effect of a polysaccharide in comparison with dextrose, which has a DE of 100. Both maltodextrins with a DE between 3 and 20 and dry glucose syrups with a DE between 20 and 37 as well as the so-called yellow dextrans and white dextrans with higher molecular weights in the range from 2000 to 30,000 g/mol can be used.

The oxidized derivatives of such dextrans are their conversion products with oxidation agents that are capable of oxidizing at least one alcohol function of the saccharide ring to a carboxylic acid function. A product oxidized at C₆ of the saccharide ring can be particularly advantageous.

Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are also other suitable cobuilders. Ethylenediamine-N,N'-disuccinate (EDDS) is preferably used in the form of its sodium or magnesium salts. Also preferred in this connection are glycerol disuccinates and glycerol trisuccinates. Appropriate amounts for use in zeolite-containing and/or silicate-containing formulations are 3-15 wt%.

Other usable organic cobuilders are, for example, acetylated hydroxycarboxylic acids or their salts, which can optionally also be in lactone form and which contain at least 4 carbon atoms and at least one hydroxy group and a maximum of two acid groups.

Another class of substances with cobuilder properties consists of the phosphonates. These compounds were already described as suitable substances for modification of the particle surface. They can also be used directly as individual substances.

Moreover, all compounds that are capable of forming complexes with alkaline earth ions can be used as cobuilders.

In addition, the agents that are produced can exhibit all of the substances that are conventional in detergents and cleaning agents such as enzymes, bleaches, bleach activators, complexing agents, antiredeposition inhibitors, foam inhibitors, inorganic salts, solvents, pH adjustors, odorants, perfume vehicles, fluorescent agents, dyes, hydrotopes, silicone oils, other soil release compounds, optical brighteners, antiredeposition inhibitors, shrinkage inhibitors, crease protection agents, color transfer inhibitors, antimicrobial agents, germicides, fungicides, antioxidants, corrosion inhibitors, antistatic agents, ironing aids, water-repellant and impregnation agents, swelling agents and antislip agents, UV absorbers or their mixtures.

Possibilities as enzymes that can be used in the agents are ones from the class of the oxidases, proteases, lipases, cutinases, amylases, pullulanases, cellulases, hemicellulases, xylanases and peroxidases as well as their mixtures, for example proteases like BLAP®, Optimase®, Opticlean®, Maxacal®, Maxapem®, Alcalase®, Esperase® and/or Savinase®, amylases like Termamyl®, Amylase-LT®, Maxamyl®, Duramyl® and/or Purafect® OxAm, lipases like Lipolase®, Lipomax®, Lumafast® and/or Lipozyme®, cellulases like Celluzyme® and/or Carezame®. Particular suitable are enzymatic agents obtained from fungi or bacteria like *Bacillus subtilis*, *Bacillus licheniformis*, *Streptomyces griseus*, *Humicola lanuginosa*, *Humicola insolens*, *Pseudomonas pseudoalcaligenes* or *Pseudomonas cepacia*. The optionally used enzymes can, as described, for example, in European Patent EP 0 564 476 or in the International Patent Application WO 94/23005, be adsorbed on carrier substances and/or embedded in coating substances, in order to protect them against premature inactivation. They are preferably contained in the agents in accordance with the invention in amounts up to 10 wt%, especially from 0.2 wt% to 2 wt%, with enzymes that had been stabilized against oxidative degradation being especially preferred.

Among the compounds that produce H_2O_2 in water and serve as bleaches sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate have particular importance. Other usable bleaches are, for example, persulfates and mixed salts with persulfates, like the salts obtainable under the trade name CAROAT®, peroxyphosphates, citrate perhydrates as well as H_2O_2 -producing peracid salts or peracids like perbenzoates, peroxyphthalates, diperazelaic acid, diperdodecanoic diacid or phthaliminoperacids like phthaliminopercaproic acid. Organic peracids, alkali perborates and/or alkali percarbonates are preferably used, in amounts from 0.1 to 40 wt%, preferably 3 to 30 wt%, especially 5 to 25 wt%.

In order to achieve an improved bleaching action when washing textiles at temperatures of 60°C and below and especially in laundry pretreatment, bleach activators can be incorporated. Compounds that under perhydrolysis conditions produce aliphatic peroxocarboxylic acids with preferably 1-10 C atoms, especially 2-4 C atoms, and/or optionally substituted perbenzoic acid, can be used as bleach activators. Substances that have O- and/or N-acyl groups with said number of carbon atoms and/or optionally substituted benzoyl groups are suitable. Preferred are polyacylated alkylenediamines, especially tetraacetylenediamine (TAED), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, especially 1,3,4,6-tetraacetylglycoluril (TAGU), N-acylimides, especially N-nonanoylsuccinimide (NOSI), acylated phenol sulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), acylated hydroxycarboxylic acids like triethyl-O-acetyl citrate (TEOC), carboxylic acid anhydrides, especially phthalic acid anhydride, isatoic acid anhydride and/or succinic acid anhydride, carboxylic acid amides like N-methyldiacetamide, glycolide, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate, isopropenyl acetate, 2,5-diacetoxy-2,5-dihydrofuran and the enol esters known from the German Patent Applications DE 196 16 693 and DE 196 16 767 and acylated sorbitol and mannitol or their mixtures described in the European Patent Application EP 0 525 239 (Sorman), acylated sugar derivatives, especially pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose as well as acetylated, optionally N-acetylated glucamine or gluconolactone, triazole or triazole derivatives and/or particulate caprolactams and/or caprolactam derivatives, preferably N-acylated lactams, for example N-benzoylcaprolactam and N-acetylcaprolactam, which are known from the International Patent Applications WO-A-94/27970, WO-A-94/28102, WO-A-94/28103, WO-A-95/00626, WO-A-95/14759 and WO-A-95/17498. The hydrophilically substituted acyl acetals known from the German Patent Application DE-A-196 16 769 and the acyl lactams described in the German Patent Application DE-A-196 16 770 and the International Patent Application WO-A-95/14075 are likewise preferably used. The combinations of conventional bleach activators known from the German Patent Application DE-A-44 43 177 can also be used. Likewise, nitrile derivatives like cyanopyridines, nitrile quats, for example N-alkylammonium acetonitriles and/or cyanamide derivatives can also be used. Preferred bleach activators are sodium 4-(octanoyloxy)benzene sulfonate, n-nonanoyl- or isononanoyloxybenzene sulfonate (n- or iso-NOBS), undecenoyloxybenzene sulfonate (UDOBS), sodium dodecanoyloxybenzene sulfonate (DOBS), decanoyloxybenzoic acid (DOBA, OBC 10) and/or dodecanoyloxybenzene sulfonate (OBS 12) and N-methylmorpholinium acetonitrile (MMA). Such bleach activators are contained in the usual amounts from 0.01 to 20 wt%, preferably in amounts from 0.1 to 15 wt%, especially 1 wt% to 10 wt%, with respect to the total composition.

The so-called bleach catalysts can also be contained in addition to the conventional bleach activators or instead of them. These substances are bleach-enhancing transition metal salts or transition metal complexes such as Mn, Fe, Co, Ru or Mo salen complexes or carbonyl complexes. Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes with N-containing tripod ligands and Co, Fe, Cu and Ru-ammine complexes are also suitable as bleach catalysts, and those compounds that are described in DE 197 09 284 A1 are preferably used.

Textile detergents can, depending on the particular formulation, be used for laundry pretreatment, for washing and for aftertreatment, for example as a softener rinse, etc. Use in an aftertreatment treatment (for example a softener rinse) can primarily improve the hydrophilicity, and not lead to a visible result until later, i.e., in a washing process that follows wearing the article.

Pretreatment agents that contain the particles used in accordance with the invention contain as additional ingredients anionic and nonionic surfactants, optionally bleaches and other components. If the pretreatment agents are in the form of a spray, as a rule they also contain solvents like petroleum spirits.

Textile detergents that are in liquid to gel form can [contain] 5-40 wt%, preferably 15-30 wt% liquid nonionic surfactants, 1-20 wt%, preferably 5-15 wt% anionic surfactants, up to 10 wt%, preferably up to 5 wt% sugar surfactants, up to 20 wt%, preferably from 5-15 wt% soaps, up to 10 wt%, preferably from 1 to 7 wt% citrate, and optionally enzymes, brighteners, dyes, perfumes, polymers (for example to prevent graying (antiredeposition agents)) and/or phosphonates.

An aftertreatment agent like a textile softener rinse contains, besides the particles used in accordance with the invention, cationic surfactants and optionally other conventional ingredients and solvents.

Examples

The improvement of soil release over the reduction of soil redeposition is determined by measuring the change of the hydrophilicity of textile surfaces. Textile strips 2 cm x 8 cm in size were stirred for 24 h in

- A water
- B 2.5% SiO₂ sol (obtained from Merck KGaA, Darmstadt, 10%)
- C 2.5% SiO₂ sol (obtained from Merck KGaA, Darmstadt, 10%) + 0.1% Sokalan® HP22 (polyethylene glycol-vinyl acetate polymer, commercial product of BASF AG)
- D 0.1% Sokalan® HP22 (polyethylene glycol-vinyl acetate polymer, commercial product of BASF AG)

Then the strips were dried and the water absorption capacity (in g) was measured. The water absorption capacity was determined with a commercial tensometer (Krüss K14). The textile samples were automatically moved toward the water surface from above until the first contact with water brought about an increase of weight detectable for the device. Then the additional weight increase was measured with the textile piece held in place for 2 min.

The measurement results are summarized in the following table, where the increase of hydrophilicity in % is given with respect to the value for treatment with water. The hydrophilicity of the textile after treatment with water was taken as 1.

	A	B	C	D
Baumwolle ①	1	13	5	-2,6
Polyester/Baumwolle ②	1	15	15	1,4

Key: 1 Cotton
2 Polyester/cotton

The measurement results show that the hydrophilicity for cotton and cotton blends can be clearly increased.

Claims

1. The use of particles with a particle size from 5 to 500 nm to improve soil release of surfaces and/or to reduce soil redeposition on surfaces.
2. A use as in Claim 1, which is characterized by the fact that the particles have a particle size from 5 to 250 nm.
3. A use as in one of Claim 1 or 2, which is characterized by the fact that the particles are selected from any precipitation silicas, aerogels, xerogels, Mg(OH)₂, boehmite (Al(O)OH), ZrO₂, ZnO, CeO₂, Fe₂O₃, Fe₃O₄, TiO₂, TiN, hydroxyapatite, bentonites, hectorite, SiO₂:CeO₂, SnO₂, In₂O₃:SnO₂, MgAl₂O₄, HfO₂, sols like SiO₂ sols, Al₂O₃ sols or TiO₂ sols, as well as mixtures of these substances.
4. A use as in one of Claims 1-3, which is characterized by the fact that the surfaces are textile surfaces and/or hard surfaces.

5. A use as in one of Claims 1-4, which is characterized by the fact that the particles are used for textile finishing, in textile detergents, for textile pretreatment or textile aftertreatment.

6. A use as in Claim 5, which is characterized by the fact that the particles are contained in the agents in an amount from 0.01 to 35 wt%, with respect to the ready-to-use agents.

7. A use as in one of Claim 5 or 6, which is characterized by the fact that the nanoscale particles are present in the application solution in an amount from 0.001 to 10 wt%, preferably from 0.01 to 2 wt%, with respect to the application solution.

8. A use as in one of Claims 5-7, which is characterized by the fact that the pH of the application solution is between 6 and 12, especially between 7 and 10.5.

9. A use as in one of Claims 1-8, which is characterized by the fact that the surfaces of the particles are modified with complexing agents selected from the phosphonates like 1-hydroxyethane-1,1-diphosphonic acid, aminotri(methylenephosphonic acid), diethylenetriamine-penta(methylenephosphonic acid) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBS-AM), which are mostly in the form of their ammonium or alkali metal salts, heavy metal complexing agents like ethylenediaminetetraacetic acid or nitrilotriacetic acid in the form of the free acids or as alkali metal salts, their derivatives, alkali metal salts of anionic polyelectrolytes like polymaleates and polysulfonates, and low molecular hydroxycarboxylic acids like citric acid, tartaric acid, malic acid, lactic acid or gluconic acid or their salts.

10. A use as in one of Claims 5-9, which is characterized by the fact that the agents contain hydrophilizing agents selected from the group of ethanol, n-propanol or isopropanol, butanols, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ethers, dipropylene glycol monomethyl or monoethyl ethers, diisopropylene glycol monomethyl or monoethyl ethers, methoxy, ethoxy or butoxytriglycols, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol t-butyl ether, alcohols, especially C₁-C₄ alkanols, glycols and polyols and polyethylene glycol that is liquid at room temperature, carboxylic acid esters and any mixtures of the said substances.

11. A use as in one of Claims 1-10, which is characterized by the fact that the particles are incorporated into agents that are in liquid to gel form or in solid form, especially powders or compacted materials like tablets.

12. A use as in one of Claims 1-11, which is characterized by the fact that surfactants, which are selected from the nonionic, anionic, amphoteric and cationic surfactants and in mixtures of them, are additionally used.

13. Agents for textile treatment which are characterized by the fact that they contain particles with a particle size from 5 to 500 nm to improve the soil release of textile surfaces and/or to reduce soil redeposition on textile surfaces.

14. An agent as in Claim 13, which is characterized by the fact that builders selected from the group of the zeolites, silicates, carbonates, organic builders and cobuilders and phosphates are contained.

15. An agent as in Claim 13 or 14, which is characterized by the fact that enzymes, bleaches, bleach activators, complexing agents, antiredeposition inhibitors, foam inhibitors, inorganic salts, solvents, pH adjustors, odorants, perfume carriers, fluorescent agents, dyes, hydrotopes, silicone oils, soil release compounds, optical brighteners, antiredeposition inhibitors [sic], shrinkage inhibitors, crease protection agents, color transfer inhibitors, antimicrobial agents, germicides, fungicides, antioxidants, corrosion inhibitors, antistatic agents, ironing aids, water repellant and impregnation agents, swelling and antislip agents, UV absorbers or their mixtures are contained.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C11D3/00 C11D3/12 D06M11/45 D06M11/46 D06M11/49		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C11D D06M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 7 August 2001		Date of mailing of the international search report 20/08/2001
Name and mailing address of the ISA European Patent Office, P.B. 5616 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer Koegler-Hoffmann, S

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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